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COMPOSITE POWDERS WITH THE PSEUDOEUTECTIC STRUCTURE IN THE Al_2O_3 – TiN SYSTEM

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The processes occurring in the synthesis of composite powders in Al_2O_3 – TiN system are considered for two variants: the first variant is the reaction of carbothermic reduction of TiO_2 mixed with Al_2O_3 with simultaneous nitration, and the second one is direct nitration of metallic titanium dispersed in aluminum oxide under high-frequency heating in a “cold” crucible. The synthesis produces submicron composite powders, which are promising for application in construction ceramics.

Transition element nitrides are rather widely used in contemporary engineering both in their pure form and in compositions with oxides, borides, and carbides.

The composite powders based on the Al_2O_3 – TiN system are used in various fields of engineering, in particular, in production of cutting instruments. The composites in such systems used to be obtained from plasmachemical ultradisperse titanium nitride powder and technical alumina. The plasmachemical synthesis of titanium nitride is environmentally undesirable because of the problems related to utilization of hydrogen chloride, which is present in the synthesis products. Therefore, the search for alternative methods for producing ultradisperse and submicron powders of this type is quite significant.

If a composite is based on high-melting compounds, the most important condition consists in the thermodynamic compatibility of the components within a wide temperature range, up to the melting point. In this case, binary systems are described by phase diagrams of the eutectic type [1], in which the natural composites, i.e., eutectics with unique sets of properties, are implemented. Furthermore, composite materials are often developed using ultradisperse components, whose structure in sintering approaches a eutectic structure in the extent of its phase boundaries [2, 3]. This technique proved efficient as well in developing composites in systems with thermodynamically incompatible components, which coexist without perceptible chemical reactions only up to certain temperatures. Thus, plasmachemical titanium nitride mixed with aluminum oxide can be used in sintering at temperature 1800–2000°C to develop cutting ceramics known as kortinite (RF Patent No. 2115756).

The eutectics in their traditional meaning are not formed in such systems; however, it is possible in their sintering to obtain analogous structures with a set of useful properties.

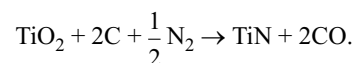
The structure of such sintered material resembles a eutectic structure in the extent of its phase boundaries and the size of the phase components. The uniformly distributed submicron grains of chemically heterogeneous phases mutually impede the growth of grains in sintering, which determines the respective structure-sensitive properties, i.e., increased strength and crack resistance.

Powdered boron carbide in [3] was obtained by direct induction heating of a solid-phase mixture of boron and coke. We used this experimental scheme for the synthesis of composite powders (RF Patent No. 2115756).

The Al_2O_3 – TiN system was selected for research. It was earlier established that the presence of TiN grains, which are uniformly distributed in the ensemble of particles, in the amount of over 20 wt. % significantly impedes the growth of Al_2O_3 grains in sintering [4, 5].

There are no fundamental obstacles to obtaining submicron TiN grains directly in a mixture of Al_2O_3 with initial reactants ensuring the synthesis of titanium nitride. Such composite can be produced by the following procedures: synthesis of titanium nitride via the reaction of carbothermal reduction of TiO_2 mixed with Al_2O_3 with simultaneous nitration, or synthesis of titanium nitride by direct nitration of metallic titanium dispersed among Al_2O_3 grains under high-frequency heating in a “cold” crucible. The synthesis produces submicron composite powders, which are promising for structural ceramics.

The reaction of titanium oxide with carbon and nitrogen can proceed as follows:



Scientists studying the high-temperature reactions of titanium oxide with carbon in a nitrogen flow do not have a common opinion of the kinetics and the mechanism of this

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process [6, 7]. Many authors believe that the effect of carbon and nitrogen on titanium oxide is implemented on the basis of higher oxides and consists of the proper reduction with active participation of gaseous carboxides and the incorporation of metalloids in oxygen vacancies. It is established that under the joint effect of carbon and nitrogen on titanium oxide, a substantial part of nitrogen is contained in the products of higher oxides reaction, in which nitrogen in the absence of a reducing agent has not been identified. The rate of the reduction process depends on the activity of the carbon material determined by the size of its particles, its quantity, specific surface area, and atomic-molecular structure. All these parameters should be taken into account in selecting a reducing agent. Of special importance is contact between the carbon particles, which is improved in compressing and, accordingly, decreases the resistivity [7, 8].

Experiments in producing composite powders in the $\text{Al}_2\text{O}_3 - \text{TiO}_2$ system were carried out using a high-frequency LD-2-60 set at frequency 5.28 MHz and effective vibration power 8.10 kW. The product was synthesized by heating the initial batch in a graphite crucible with slit walls (in this way the "cold crucible" principle was implemented).

The initial components were titanium dioxide (rutile), lamp soot, technical titanium, aluminum oxide of various grades, and nitrogen.

The batch was prepared in accordance with the selected schemes, then mixed and milled in a vibration mill for 1 h. The last stage of the batch preparation was its compression in tablets. The temperature in the course of synthesis was monitored by a Promin' pyrometer.

Lamp soot was the selected carbonaceous reducing agent, as this soot has certain advantages over other soot varieties in its content of ash residue, volatile impurities, moisture, etc.

The beginning of the reaction of carbothermal reduction with simultaneous nitration was indicated by gas emission from a hole in the bottom of the reactor in the form of a flame tongue caused by carbon oxide burning in air, which started on reaching 1500°C . Approximately 25–30 min after power was supplied, the gas emission stopped. The gas emission intensity was constant in the course of synthesis, but the beginning of the process was characterized by a short induction period, which is presumably related to difficult adsorption of gaseous carbon oxide on titanium oxide particles. The maximum temperature on the charging surface reached 1880°C at 8 kW power. The synthesis products (sintered cakes) were studied with a DRON-3 x-ray diffractometer with CuK_α radiation. The x-ray phase analysis established that the carbothermal synthesis of $\text{Al}_2\text{O}_3 - \text{TiN}$ composite powder proceeds via metalloid compounds with the titanium oxide structure. The end product is the binary system $\text{Al}_2\text{O}_3 - \text{TiN}$.

Another method for producing composite powders in the $\text{Al}_2\text{O}_3 - \text{TiN}$ system is direct nitration of powdered titanium dispersed in aluminum oxide. The initial batch was mixed in a certain ratio and milled in a vibration mill for 1 h. The ex-

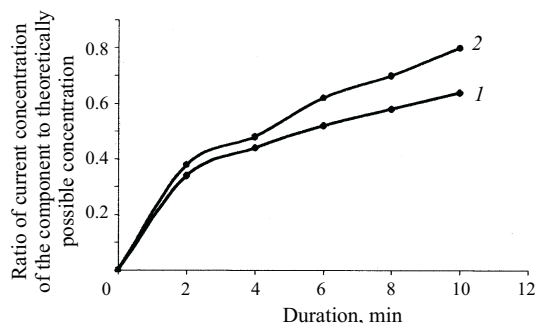


Fig. 1. Kinetics of titanium nitride formation from metallic titanium dispersed among aluminum oxides grains of "chemically pure" grade (1) and of spectral purity (2) under charging surface temperature 1800°C .

periments in nitration in the induction-heater of a high-frequency plant were conducted both with tablets and with the batch freely poured into the crucible under an effective vibration power equal to 8 kW. The cake produced from the freely poured batch can be arbitrarily divided into three zones: the central porous one (near the geometrical axis of the induction heater) colored golden, the intermediate one having brown color, and the peripheral zone that is colored gray. The data of x-ray phase analysis indicated that the central and the intermediate zones consist of $\alpha\text{-Al}_2\text{O}_3$ and TiN, and the peripheral zone contains not only $\alpha\text{-Al}_2\text{O}_3$ and TiN, but Ti as well.

The synthesis of a batch preliminarily compressed in tablets yielded slightly different results. The sintered cake in its cross-section had a homogeneous brown color. Such samples were obtained for mixtures with aluminum oxide of "chemically pure" grade (which consisted of large aggregates of γ - and $\alpha\text{-Al}_2\text{O}_3$) and "spectral purity" aluminum oxide (fine-grained $\alpha\text{-Al}_2\text{O}_3$ powder). The kinetics of TiN formation is shown in Fig. 1. The degree of transformation was determined from the weight increment (in accordance with the reaction $2\text{Ti} + \text{N}_2 \rightarrow 2\text{TiN}$). As the result of the experiment, the minimum duration of synthesis was found to be 3 min. A longer treatment led to the formation of a denser cake, which was difficult to mill.

The cakes obtained by direct nitration of a tableted mixture of titanium and aluminum oxide powders of various degrees of dispersion were crushed and milled in ethyl alcohol in a vibration mill for 40 h. The composite powders were molded in a high pressure chamber (1800°C , 3.4 GPa). The microstructure of compact samples was studied on polished sections using an AVT-55 scanning electron microscope. The image processing made it possible to reveal the size distribution of titanium nitride grains among aluminum oxide grains (Fig. 2), and this analysis demonstrated that although the average size of titanium nitride grains is close ($0.5 \mu\text{m}$), the size dispersion is significantly different. This is presumably related to the mechanism of titanium nitride formation in the conditions of the experiments, but also depends on the size and the state of aluminum oxide surface.

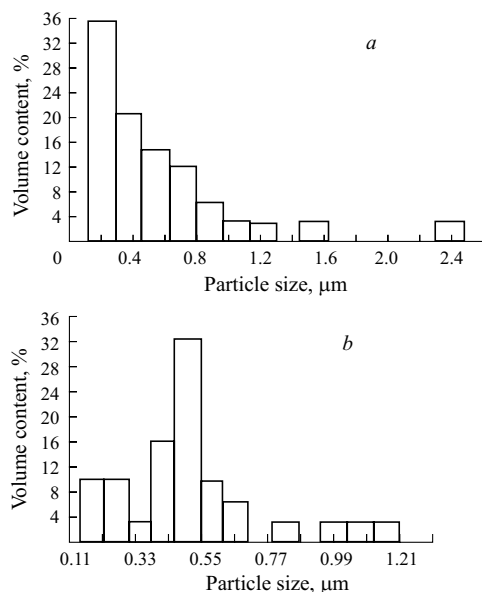


Fig. 2. Size distribution of titanium nitride grains among aluminum oxide grains of grade “chemically pure” (a) and spectrally pure (b) in sintered sample.

The data on the specific surface area of aluminum oxide (135 m²/g for “spectral purity” Al₂O₃ and 69.6 m²/g for Al₂O₃ “analytical grade”) suggest that the spectral-pure aluminum oxide consists of aggregates which disintegrate in milling in the course of titanium nitride formation.

Additional studies investigated the behavior of melted metal drops arising in heating of the mixture of titanium with aluminum oxide. The dispersion of melted titanium proceeds in the aluminum oxide matrix. The considered matrix was aluminum oxide of grades M1, M5, and M14, different in particle size and the surface state. Heating was carried out in a “cold” crucible on a high-frequency plant without supplying nitrogen. Finely disperse titanium homogeneously distributed among the grain of the dielectric (aluminum oxide) in the high frequency field rapidly reaches the melting point (1720°C) and spreads over the surface of the adjacent oxide grains, which leads to the fragmentation of the drops.

The samples after melting were investigated employing a scanning electron microscope. As a consequence of intense heating of the sample in the high-frequency field up to the melting point, the metal melts with the formation of surface microfilms, which later under the effect of surface tension disintegrate into microdrops (Fig. 3). It can be assumed that microdrops and microfilms react with the gaseous nitrogen flow and form isometric titanium nitride grains. The enthalpy of this nitration reaction is very high and constitutes 120 kJ/mole at temperature 1700°C, which additionally heats the system.

The obtained results indicate that the size of titanium nitride grains, which are formed as a consequence of nitration of microdrops, directly depends on the size and the surface state of the oxide. The minimum size of titanium

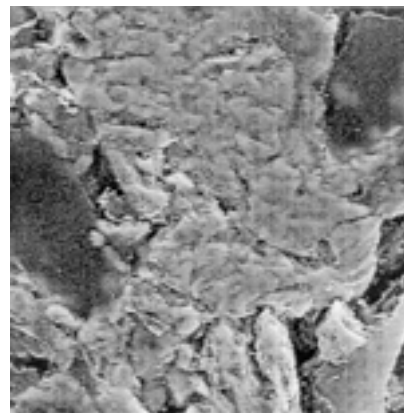


Fig. 3. Microstructure of samples of the composition 50% Al₂O₃ (M5) – 50% Ti (volume content) exposed for 4 min in an induction furnace without nitrogen supply (× 1000).

microdrops was obtained in mixtures with aluminum oxide M14. Titanium microdrops and, accordingly, titanium nitride grains do not coalesce, as they are spatially divided by oxide particles. Thus, the granulometry of titanium nitride grains is a derivative of the granulometry of aluminum oxide as the matrix phase.

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